Greek Letters

α_j = coefficients defined in Eq. 24
γ = parameter defined in Eq. 21
ϵ = parameter defined in Eq. 14
ϵ_b = bed voidage
ϵ_p = pellet voidage
λ = ratio of reactant molecular size to pore size
ρ_p = pellet density
τ = tortuosity factor
ϕ_o = parameter defined in Eq. 14
Ω = nondimensional reaction rate defined in Eq. 18
ζ = nondimensional distance along the reactor

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Manuscript received March 2, 1983; revision received May 19, and accepted May 31, 1983.

Decomposition Strategy for the Synthesis of Minimum-Unit Heat Exchanger Networks

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INTRODUCTION

The heat exchanger network synthesis problem has been reviewed by Nishida et al. (1981). We consider the problem with n_h hot streams and n_c cold streams, each with given flow rate, heat capacity, inlet and target temperatures. We adopt the terminology and notation of Flower and Linnhoff (1980) and Nishida et al. (1981).

In previous work, the "minimum number" of heaters, coolers, and exchangers required to solve the problem, n_{min}, is given as one less than the total number of streams and services (Hohmann, 1971):

$$n_{min} = n_h + n_{hs} + n_c + n_{cs} - 1 \tag{1}$$

where

n_{cs} = number of hot services

n_{hs} = number of cold services

Flower and Linnhoff note that when heat recovery demands are stringent, i.e., when heat is to be transferred between streams across a small temperature difference, the minimum number of exchangers may be larger than this. Flower and Linnhoff also note that occasionally a solution may be produced which exhibits fewer units than this "minimum" number, and they give an example solution for 10SP1 exhibiting only nine units. In this work the conditions under which such solutions can be produced are explored, and a strategy for locating them efficiently is proposed.

Linnhoff et al. (1979) illustrate the manner in which the number of heat exchanger units in a solution can be reduced by dividing the problem into two separate components. In this work such a strategy is adopted and applied to a problem of unprecedented size and is found to yield desirable benefits from a design and operability standpoint.

ADVANTAGES OF THIS METHOD

The Decomposition Strategy yields these benefits:

1) Solutions are produced containing fewer heat exchangers for a given problem than would be expected based on Eq. 1.

2) Very large reductions in computational difficulty are realized, facilitating the solution of large problems with 20 streams or more.

3) Actual designs based on the resulting solutions exhibit modularity and independent operation, simplifying controllability.

ESTABLISHING THE MINIMUM NUMBER OF EXCHANGERS

If we ignore the heat loads, temperature compatibilities, etc., of the hot and cold streams, leaving only the requirement that every stream be matched at least once, the minimum number of exchangers required is only as large as the larger of the set of hot

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streams and hot utilities or the set of cold streams and cold utilities. This can be thought of as the "absolute" minimum number of exchangers. For example, in the 10SP1 problem, which has five cold process streams and requires one cold utility stream, the "minimum" number of exchangers by Eq. 1 is ten, but the "absolute" minimum number of exchangers is six. When the stream temperatures and heat loads are considered, it is readily seen to be impossible to produce a solution to 10SP1 with six exchangers. However, it is worthwhile to devise a strategy which deliberately seeks to approach this "absolute" minimum. What is sought is a division of the complete problem into two or more completely independent problems, through the location of matched subsets of hot and cold streams, with the addition of an appropriate utility to the remainder to accomodate the resulting imbalance. When preanalysis has identified a "pinch" in the original problem, efficient solutions will already have the form of two disconnected networks, each of which will contain a utility of opposite type.

PERFORMING THE HEAT LOAD MATCHING

To locate subsets of the hot and cold streams whose heat loads match, we must perform an exhaustive enumeration and comparison of all the combinations of streams on each side. Because the stream heat loads are independent of each other, it is highly unlikely in general that an exactly matched pair of subsets of the hot and cold streams can be found. However, for problems with ten or more process streams, a surprisingly large number of pairs of subsets can usually be found which agree within some arbitrary tolerance, say 1%. This inexact match can be made exact by adjusting the stream target temperatures as necessary. For example, when two matched subsets agree to within 0.5% of their total duty, the target temperature of each stream must typically be adjusted about 0.5 K.

STEPS IN THE DECOMPOSITION METHOD

1) Construct the composite heat availability lines for the original problem. If the problem contains a "pinch," immediately decompose it into two halves above and below the "pinch" (Linnhoff, 1980) and proceed to Step 5. If the problem does not contain a "pinch," continue with Step 2.

2) Generate all 2^{n_h} subsets of the hot streams and record a total heat load for each. Each subset we shall call a "partition;" the remainder corresponding to each partition is its "complement." Perform the same for the cold streams.

3) Exhaustively compare the heat loads of the hot and cold partitions generated in Step 2. Record all pairs whose heat loads agree to within the arbitrarily selected tolerance.

4) Construct the composite heat availability lines for the subproblems consisting of matched pairs of partitions and their matched complements. Record all instances where both exhibit minimum temperature differences exceeding the heat recovery approach temperature specified in the problem.

5) If the number of streams in a subproblem is "large," consider decomposing it further by returning to Step 2.

6) For each decomposition whose subproblems pass Step 4, balance the heat loads by adjusting the stream target temperatures slightly, according to some suitable method. Those subproblems which remain following removal of matched partitions from an imbalanced original problem will usually require the addition of a utility stream, removing the need to modify target temperatures.

7) Attempt to construct network solutions on the balanced subproblems, each of which exhibits the "minimum number of units." For a particular decomposition scheme to be valid, all its subproblems must yield solutions with the appropriate "minimum number of units."

8) Select the best decomposition schemes based on cost of the resulting solutions or other criteria. Consider generating more solutions by accepting a less strict tolerance in Step 3.

The details of the algorithm used to partition the larger problem and to locate heat-balanced subproblems will be presented in a forthcoming paper. This paper will also contain further information on the enumeration of solutions.

TABLE 1. DATA FOR PROBLEM 23SP1

	Supply Temp.	Target Temp.	Heat Capacity Flow Rate W/K
Cold Streams			
1	323	423	7,620
2	389	495	6,080
3	311	494	8,440
4	355	450	17,280
5	366	478	13,900
6	311	490	8,440
7	350	450	17,280
8	352	468	13,900
9	366	478	8,440
10	311	489	8,440
11	422	478	21,780
12	339	411	13,840
Hot Streams			
1	433	366	8,790
2	522	411	10,550
3	510	349	14,770
4	544	422	12,560
5	472	339	17,730
6	505	339	14,770
7	544	420	12,560
8	475	339	17,730
9	583	478	12,530
10	517	366	8,320
11	511	339	6,960

COMMENTS ON THE PROBLEM 23SP1

The problem size was selected to be sufficiently large to preclude efficient solution by any of the existing methods, as well as to allow a large number of heat-balanced subproblems to be generated. The problem data are obtained from combining the existing literature problems 10SP1, 6SP1, and 7SP2. It should be noted that each of these problems is unbalanced; therefore, the Decomposition Method will not perform the trivial disconnection of 23SP1 into the original problems. The stream data are further modified to eliminate identical streams and to relax slightly the heat recovery demanded. 23SP1 does not exhibit a "pinch," so it requires only a single cold utility.

23SP1 was first subjected to a decomposition into pairs of subproblems, Figure 1. The number of combinations for the twelve cold streams is $2^{12} = 4{,}096$. For the hot streams there are $2^{11} = 2{,}048$, giving a total of $2^{23} = 8{,}388{,}608$ ways to decompose the problem. Because this is such a large number, matched components were required to agree in heat load to a tolerance of 0.000001. The algorithm found 18 ways to decompose the problem satisfying this degree of heat load balance as well as the heat recovery approach temperature constraint of 10 K. This level of agreement was close enough that no streams had to have target temperatures reassigned within the precision of the data. Such agreement should be characteristic of large problems with relatively easy heat recovery.

After the primary decomposition was performed, many resulting subproblems were within reach of solution by existing efficient methods. A secondary decomposition was performed to reduce even further the number of exchangers required in the final solution. In some promising cases, both the matched primary partitions and their complements were decomposed again, dividing the initial problem into four subproblems. Because the secondary decompositions were performed on subproblems with fewer streams, it was necessary to relax the agreement in heat loads at this stage to

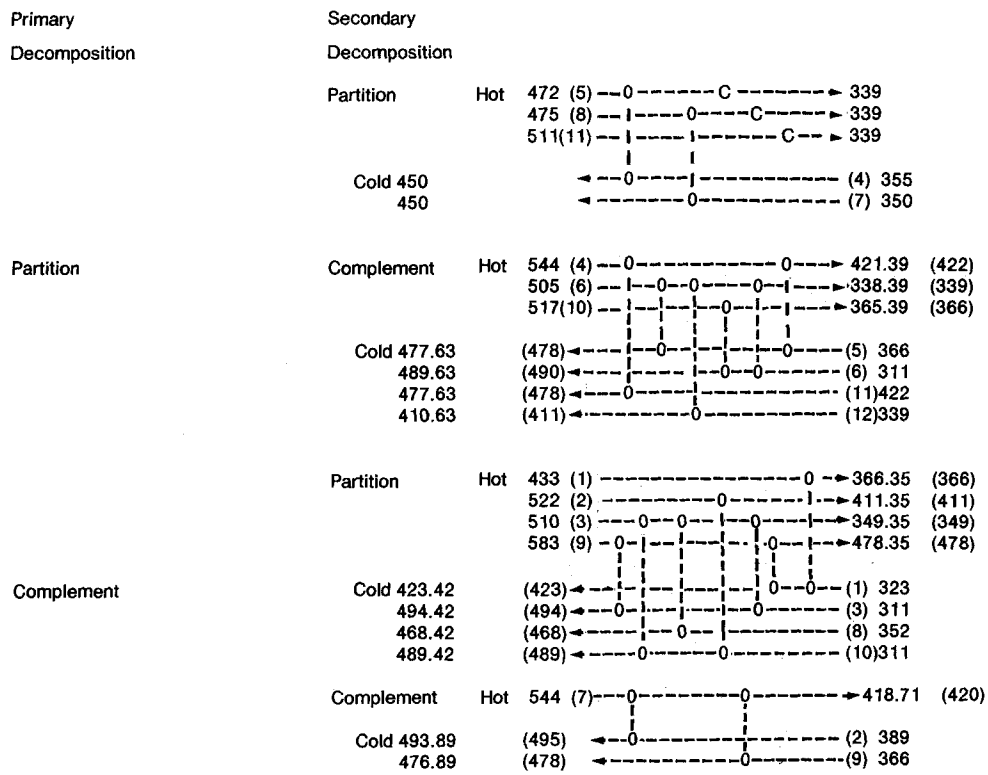

Figure 1. Solution for 23SP1: component networks.

0.01 in order to generate enough candidates for network construction. An example solution for 23SP1 divided into four components, each exhibiting the "minimum number of units" is given. Note that the cold utility appears in only one component, and that the streams in the other three components have all their target temperatures reassigned. In the reassignment, the heat load imbalance was divided evenly on both sides; therefore, some streams *slightly* exceed their target temperatures while others slightly fail to reach theirs. In industrial problems, a more likely scenario would be one in which an acceptable temperature tolerance is assigned to every stream with the heat load balancing done in such a way as to minimize the temperature reassignment of constrained streams. In this solution, the maximum deviation was exhibited by hot stream 7, which exceeds its target temperature by 1.29 K. For clarity, the independent components of the networks are drawn separately in Figure 1. No attempt was made to perform an exhaustive search for all solutions, nor was any attempt at "optimization" (other than the approach to the minimum number of units) made. The solution as shown requires only 19 exchangers, four less than the 23 minimum required in a fully connected solution. It may be possible to produce a solution with fewer exchangers at the level of heat load balance used here; it is surely possible to do so at some less stringent level.

NOTATION

n_c = number of cold process streams
n_{cs} = number of cold services (utilities)
n_h = number of hot process streams
n_{hs} = number of hot services (utilities)
$n_{\min}$ = minimum number of exchangers
$T(m,n)$ = number of vertex-labeled bipartite trees on m and n points
$\deg v_i$ = number of edges incident with the point v_i in a graph; in this work, it represents the number of exchangers through which the ith stream passes

APPENDIX: ENUMERATION OF POSSIBLE SOLUTIONS

A heat exchanger network exhibiting the minimum number of exchangers by Eq. 1 will almost always have a structure identified in graph theory as a "bipartite tree." Its two partite sets consist of the hot streams (both process and utilities) and the cold streams. Scoins (1962) derives a simple formula for the number of vertex-labeled bipartite trees:

$$T(m,n) = m^{n-1}n^{m-1} \tag{2}$$

where
$T(m,n)$ = number of nonidentical trees
m,n = number of vertices in the first and second partite sets, respectively

In our case, with $n_h + n_{hs} = m$ and $n_c + n_{cs} = n$, we have:

$$T(n_h + n_{hs}, n_c + n_{cs}) = (n_h + n_{hs})^{(n_c+n_{cs}-1)}(n_c + n_{cs})^{(n_h+n_{hs}-1)} \tag{3}$$

Each tree found in Eq. 3 represents the structure shared by a number of specific networks, which are in turn determined when an ordering is assigned to multiple edges (exchangers) incident with each vertex (stream). The number of edges incident with a point v_i is called the degree of v_i, denoted $\deg v_i$. Because we will have $(\deg v_i)!$ choices for the ordering of the edges incident with each vertex v_i, we have a total number of specific networks sharing a given structure (i.e., a vertex-labeled tree) equal to:

$$T_{\text{specific}} = \prod_{i=1}^{n_s=n_h+n_{hs}+n_c+n_{cs}-1} (\deg v_i)! \tag{4}$$

This number grows rapidly with the number of streams, particularly when solutions have points of high degree.

The foregoing is in accord with the enumeration strategy of Flower and Linnhoff (1980) with the exception of Eq. 3 introduced here, which is a better lower estimate on the upper bound of candidate solution structures. The corresponding equation given by Flower and Linnhoff (1980), while forbidding hot utility-cold utility matches (which Eq. 3 does not), does not recognize the fact that solutions are trees (Flower and Linnhoff's "topological feasi-

bility"). In other words, Flower and Linnhoff's equation counts a number of networks which contain both cycles and unmatched streams, as the authors recognize. Of course, when a problem has only one utility, as is frequently the case, no trees involving hot utility-cold utility matches are counted by Eq. 3.

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Manuscript received October 18, 1982, and accepted April 15, 1983.

Gas Transport within the Developed Pore Structure of Reactive Porous Matrices

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INTRODUCTION

Heterogeneous gas-solid reactions where the reactive solid surfaces exist in micropores throughout solid pellets are commonplace to chemical engineers. A common observation is that the reactivity of an individual pellet varies with time. Indeed, at very high temperatures individual pellets internally melt and "deadburn," thereby totally eliminating internal microporous reactivity. This sintering phenomenon may also occur to lesser extents at lower reaction temperatures and would be expected to be most important for relatively high temperature reactions. One particular example of a high temperature reaction is sulfur dioxide capture by calcined calcium carbonate (limestone or dolomite) in fluidized bed combustion.

This paper presents experimental measurements of effective diffusivity of inert gases through a reactive porous matrix as a function of time and temperature. An empirical correlation is obtained which should be of value in modeling heterogeneous chemical reactions and in understanding the mechanisms of the changes in internal micropore structure. Previous studies have measured effective diffusivity at a single time and, therefore, have neglected this sintering phenomenon.

The system chosen is that of a natural calcium carbonate limestone which first decomposes, called calcination, giving off 44% of the $CaCO_3$ weight as CO_2 and yielding a reactive matrix of microporous calcium oxide with a porosity of about 0.45. Calcination dissociation proceeds gradually from the outside surface of the individual particle inward (Boynton, 1966). The developed mircoporous structure is reactive to acidic gas components such as SO_2, H_2S and CO_2.

Other investigators have studied this system but all used reactive CO_2 rather than an inert gas in their study, and none studied the system as a function of time. Campbell et al. (1970) fabricated *individual* particles from powdered $CaCO_3$ in a press. After calcination they found that the effective diffusivity of CO_2 through porous CaO ranged from 0.08 to 0.28 $cm^2 \cdot s^{-1}$ for porosities of 0.4–0.8 for temperatures between 870 and 950°C. They concluded that Knudsen diffusion predominated. Hills (1968) obtained the following empirical correlation for the effective diffusivity of CO_2 through porous CaO:

$$D_e = a + b(T - 1{,}103.15) \tag{1}$$

where $a = 0.083 \pm 0.002$ $cm^2 \cdot s^{-1}$, $b = 0.000210 \pm 0.000003$ $cm^2 \cdot s^{-1} \cdot K^{-1}$, and T is the calcination temperature. Satterfield (1970) combined the Knudsen equation with the parallel pore model to obtain the following equation to estimate the effective diffusivity of gases through porous solids:

$$D_e = 19{,}400 \frac{\epsilon^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \tag{2}$$

EXPERIMENTAL METHOD

A cylindrical pellet (typically 0.31cm thick by 2.1 cm diameter) was manufactured using a diamond coring drill bit and a carborundum saw The limestone used (Greer Limestone Co., Morgantown, WV) had an average calcium carbonate content of 75%. This pellet was mounted in a specially designed high temperature diffusion cell (Bardakci, 1980, Bardakci and Gasner, 1981) using the same principle as that of Wicke and Kallenbach (1941). The diffusion cell reactor was mounted in a tube furnace which was controlled to a selected fixed temperature. Argon gas flowed radially across one face of the pellet while nitrogen gas flowed radially across the other face. The temperature was measured at each pellet face. The differential pressure between the two sides of the pellet was maintained at 0.00 ± 0.03 cm. of water by computer control. The computer also measured and controlled flow rates and absolute pressure of each stream. In addition, it automatically injected samples from each stream into a gas chromatograph, integrated the output, and calculated many things including the effective diffusivity of argon and nitrogen through the reactive microporous pellet.